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## Film Characterization of Cu Diffusion Barrier Dielectrics for 90nm and 65nm Technology Node Cu Interconnects

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### Abstract

This paper describes film characterization of Cu diffusion barrier SiC, SiCN and SiCO in detail. Although SiCN and SiCO achieve reduced leakage current and k-value, the biggest challenge is to achieve robust stability in film stress and k value because undesirable N and O doping cause increased film stress and k value after deposition. Fine-tuned SiC makes it possible to greatly reduce leakage current and k value to 3.9. From Bias Temperature Stress (BTS) measurement, our desired SiCN, SiCO and fine-tuned SiC are assured in 10-year durability to electrical Cu diffusion.

### Introduction

To reduce the RC-delay, Inter-Metal Dielectrics (IMD's) with lower k-values have been extensively demonstrated. However, recent challenges to Ultra Low-k (ULK) integration reveal that the degraded mechanical strength of ULK causes undesirable issues in CMP and packaging processes [1-3].

Implementations of Cu diffusion barrier dielectrics with lower k-values are also effective in reducing interconnect capacitances. In fact, Cu diffusion barrier SiC that is the successor to SiN in 130nm to 90nm nodes has contributed to the great reduction of interconnect capacitances [4]. These results indicate that it is very important to reduce both k-values of IMD and Cu diffusion barrier dielectric with an acceptable mechanical strength.

In this paper, we describe film characterization of Cu diffusion barrier SiC, SiCN and SiCO in detail, and suggest the desired film concepts for successful Cu/Low-k interconnects in 90nm technology node and beyond.

### Experimental

A conventional parallel plate plasma CVD system was used for deposition of SiC, SiCN and SiCO films. Gas mixture of 4MS (Tetramethylsilane) and He was employed with NH<sub>3</sub>, Oxidant-A (Ox-A) and Oxidant-B (Ox-B), which were doped to deposit SiCN, SiCO-A and SiCO-B, respectively.

The thickness and refractive index were measured using Spectroscopic Ellipsometry, FT-IR(Fourier Transform Infrared Spectroscopy), XPS(X-ray Photoelectron

Spectroscopy) and RBS (Rutherford Backscattering Spectroscopy) were used to analyze chemical bonding of film. Hg probe was employed for measurements of k-value and leakage current. BTS measurement was carried out by using HP4156C and semi-auto probing system with a heated wafer susceptor in the temperature range of 150-250 degree C. The sample structure we used is a MIS capacitor of AlCu (300nm) / Cu (300nm) / SiC (50nm) / n-type Si. AlCu cap is needed to avoid oxidation of Cu. For this measurement, time to breakdown failure (Tbd), which is defined as when leakage current is up to 1mA, is measured by applying a positive voltage to top metal electrode. Positive electric field provides the injection of ionized Cu into dielectrics. In addition, Tbd under the condition of actual device operation (125 degree C, 0.3MV/cm) is estimated from the electric-field and temperature dependence, and 10-year durability to electrical Cu diffusion is discussed.

### Results and Discussions

#### A. Overview of film properties

Film properties of Cu diffusion barrier dielectrics, including pre-optimized SiC, SiCN, SiCO-A and low leakage SiC (LL-SiC) are summarized in Table I. The pre-optimized SiC has higher leakage current and k-value than those of other films. To improve these electrical issues, as reported previously, N or O doped films, SiCN and SiCO, achieve reduced leakage current and k-value [5-6]. SiCN and SiCO-A deposited by our desired recipes indeed have good electrical film properties, but the biggest challenge is to achieve good stability in film stress and k value because undesirable N and O doping cause increased film stress and k value after deposition. These unique film properties are additionally discussed in the next sections.

LL-SiC is one of the solutions to achieving advanced Cu diffusion barrier dielectric with lower k-value. Fine-tuned process recipe makes it possible to greatly reduce leakage current and k value to 3.9, as compared with the pre-optimized SiC. I-V curves of SiC, SiCN, SiCO-A and LL-SiC are shown in Fig. 1. Leakage current of LL-SiC is slightly higher than those of SiCN and SiCO-A when applying a high electric field. The further optimization is needed to reduce leakage current.

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### B. SiCN film characterization

In this section, film characterization and optimization of SiCN are discussed in detail. Higher NH<sub>3</sub> flow rate results in lower leakage current and k value (Fig.2). But, higher NH<sub>3</sub> flow rate causes instabilities in film stress and k value (Fig. 3). In order to obtain the stable film properties, it is very important to keep film stress in higher compressive stress than -200MPa.

In order to confirm the variation in film composition for stable and unstable SiCN, XPS analysis was applied. The oxygen concentration of unstable SiCN obviously increases after 50 days exposure to clean room air, while there is almost no change in the oxygen concentration of stable SiCN (Fig.4). These results indicate that oxidization due to the air-exposure causes unstable film properties.

### C. SiCO film characterization

Film properties of different SiCO's are summarized in Table II. All SiCO films deposited by using Ox-B have unstable film stresses and k values. These instabilities may be due to low film stress as is the case with SiCN. It is hard to condition film stress in higher compressive stress than -200MPa when using Ox-B in this study. On the other hand, it is easy to obtain high film stress by using Ox-A, resulting in good stability in film stress and k value.

In order to comprehend the effect of oxidant gas on film properties, FT-IR analysis was carried out. Figure 5 summarizes the peak height of Si-CH<sub>3</sub>, Si-O and Si-C for all SiCO films. Si-CH<sub>3</sub> peak heights of the SiCO-A family are smaller than those of the SiCO-B family. These results suggest that the Ox-A is more oxidative gas to 4MS than Ox-B. Ox-A easily oxidizes with 4MS and efficiently eliminates CH<sub>3</sub> groups out of film, resulting in highly densified film with high film stress. RBS measurements confirmed that film densities of SiCO-A and SiCO-B are 2.1 and 1.8g/cc.

Photo resist poisoning is the toughest challenge in via-first dual damascene integration. As previous papers have already reported, it is important to suppress the generation of amino species by removing N contaminant [6]. In this study, it is confirmed that N-free SiCO is preferable to SiCN as shown in Fig. 6.

### D. Cu diffusion barrier properties

Cu diffusion barrier properties were evaluated by BTS. Figure 7 shows the dependence of Tbd on applied electric field at 200 degree C for SiC, SiCN, SiCO-A, SiCO-B and LL-SiC. Similar gradients for all fitted lines indicate that dielectric breakdown failure is due to the same mechanism. From the extrapolation of fitted lines to 0.3MV/cm, estimated Tbd's are ranked as SiCO-A=SiCO-B>LL-SiC >SiCN>SiC.

Figure 8 shows the dependence of Tbd on applied electric field at 200 degree C for the different SiCO's listed in Table II. Different gradients for fitted lines indicate that dielectric breakdown failure is due to different mechanisms.

In order to judge 10-year durability to electrical Cu diffusion under the condition of actual device operation, thermal activation energy was estimated. Figure 9 shows cumulative failure distributions of Tbd for SiCN at various temperatures and Arrhenius plots of 50%TTF. Table III summarizes the estimation result of thermal activation energy, target Tbd of 10-year actual device operation and extrapolated Tbd for various dielectrics. SiCN, SiCO-A and LL-SiC are assured in 10-year durability to electrical Cu diffusion except for pre-optimized SiC.

### Conclusion

We have investigated film properties of Cu diffusion barrier dielectrics. Although doping processes of N, O into SiC reduce leakage current and k-value, it is required to achieve robust stability in film stress and k-value. For SiCN, it is important to keep film stress in higher compressive stress than -200MPa by optimizing the NH<sub>3</sub> flow rate, while the key to SiCO deposition is oxidant gas which is oxidative to 4MS and results in highly densified film with high film stress. Fine-tuned LL-SiC, which is one of the solutions to advanced Cu diffusion barrier dielectric with lower k-value, makes it possible to greatly reduce leakage current and k value to 3.9. From BTS results, our desired SiCN, SiCO and LL-SiC are assured in 10-year durability to electrical Cu diffusion.

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### References

- [1] S. Lin, et al. *Proceedings of IITC2001*, pp146-148.
- [2] J. C. Lin, et al. *Proceedings of IITC2002*, pp48-50.
- [3] M. Rasco, et al. *Proceedings of IITC2002*, pp113-115.
- [4] H. Aoki, et al. *IEDM Tech. Dig.*, 2001, pp76-79.
- [5] C.C Chiang, et al. *Proceedings of IITC2002*, pp200-202.
- [6] W. D. Gray, et al. to be published *Advanced Metal Conf.*, 2002.

Table I Film properties of Cu diffusion barrier dielectrics

Film	SiC	SiCN	SiCO-A	LL-SiC
Gas Chemistry	4MS NH <sub>3</sub>	4MS Ox-A	4MS Ox-A	4MS
Refractive Index	2.13	1.87	1.79	2.05
Stress (MPa) stability	-100 stable	-200 stable	-245 stable	-60 stable
k-value stability	5.4 stable	4.8 stable	4.5 stable	3.9 stable
Leakage Current (A/cm <sup>2</sup> ) (@2MV/cm)	2.1E-4	1.1E-8	5.0E-8	2.1E-7
Tbd (sec) (@200degC, 0.3MV/cm)	3.0E6	1.1E8	2.0E10	4.7E8

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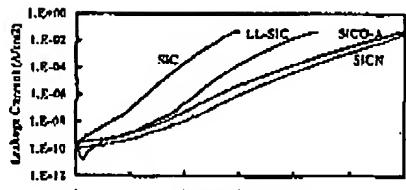


Fig. 1. I-V characteristics of SiC, LL-SiC, SiCN and SiCO-A.

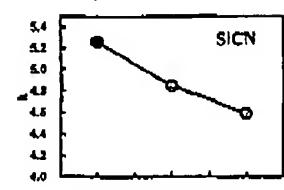


Fig. 2. k and leakage current of SiCN. Higher NH3 flow rate results in lower k value and leakage current.

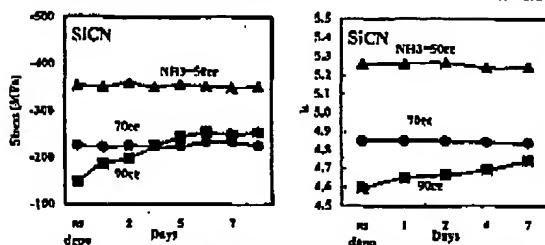


Fig. 3. Changes of stress and k value for SiCN. Higher NH3 flow rate causes instabilities in film stress and k.

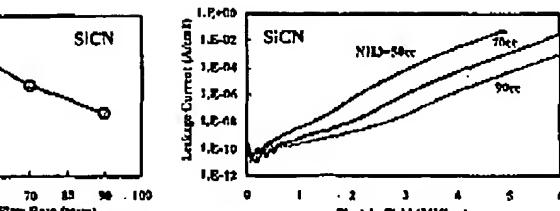


Fig. 4. Film composition of SiCN measured by XPS. O concentration of unstable SiCN increases after 50 days.

Film	SiCO-A	SiCO-A1	SiCO-A2	SiCO-B	SiCO-B1	SiCO-B2
Gas Chemistry	4MS + He + Ox-A					
Refractive Index	1.79	1.82	1.85	1.79	1.82	1.85
Stress (MPa) stability	-245 stable	-230 stable	-215 stable	+140 increased	-120 increased	+135 increased
k-value stability	4.5 stable	4.6 stable	4.6 stable	4.5 slightly increased	4.0 slightly increased	4.7 slightly increased
Leakage Current (A/cm²) (@2MV/cm)	5.0E-8	3.0E-7	4.0E-7	1.5E-8	2.0E-8	1.7E-7
Tbd (sec) (@200degC, 0.3MV/cm)	2.0E10	1.1E7	3.0E6	2.0E10	1.2E4	4.6E8



Fig. 5. PR-polishing for SiCN and SiCO. N-free SiCO is preferable to SiCN.

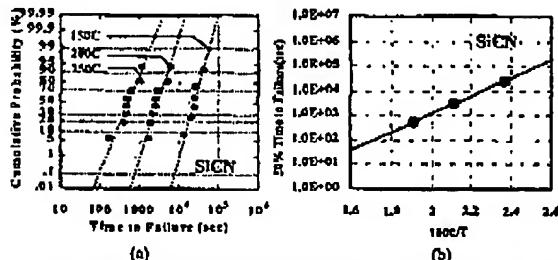


Fig. 6. (a) Cumulative failure distribution of Tbd for SiCN at various temperatures and (b) Arrhenius plots of 50% TTF.

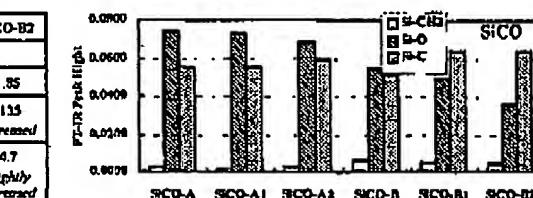


Fig. 7. FT-IR peak height of SiCO. Ox-A easily oxidizes with 4MS and efficiently eliminates CH3 groups out of SiM.

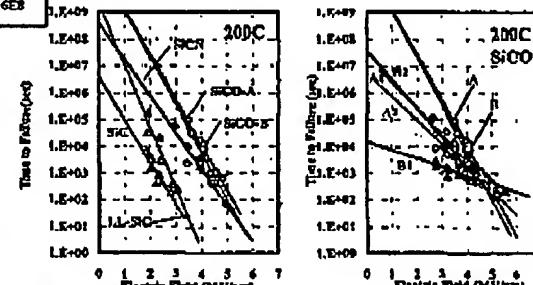


Fig. 8. Dependence of Tbd on applied electric field at 200 degree C, for various SiC.

Film	Ea (eV)	Target Tbd on 10 years @200degC (sec)	Tbd (sec)	Judge
SiC	0.78	8.4E8	3.0E6	NG
SiCN	0.73	1.1E7	1.1E7	OK
SiCO-A	0.73	1.1E7	2.0E10	OK
LL-SiC	0.90	3.7E6	4.7E3	OK